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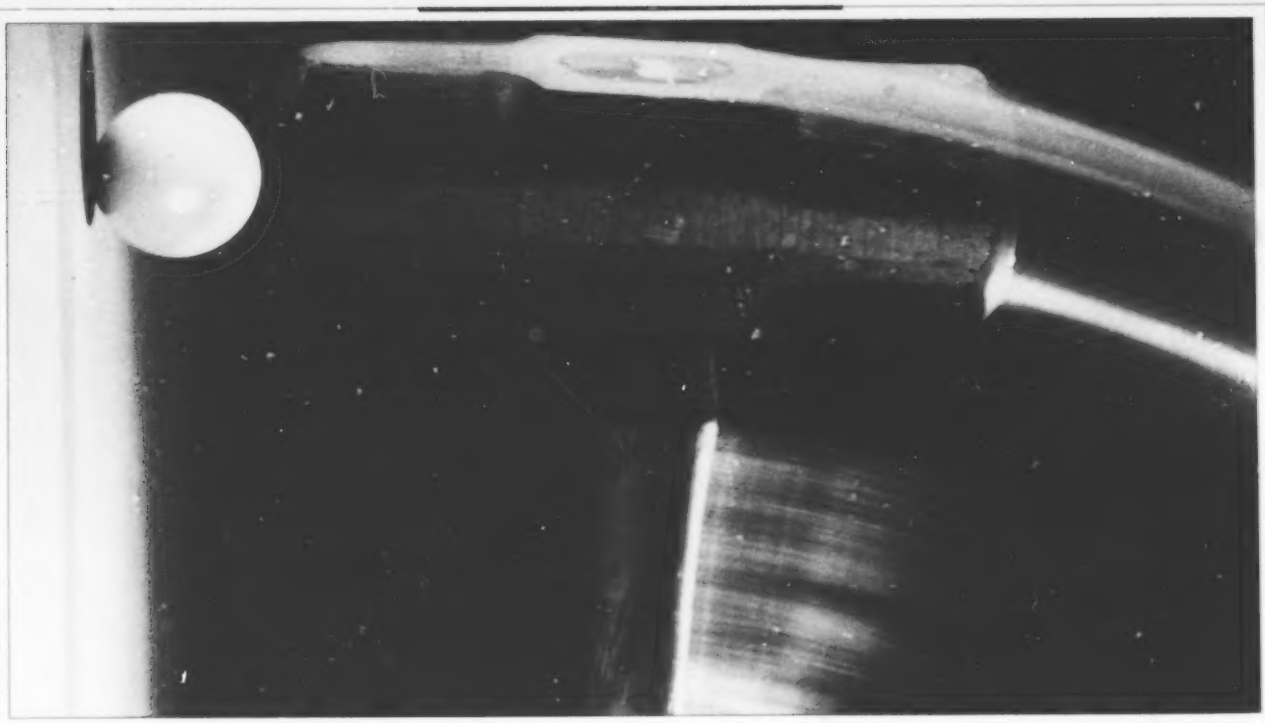

ZIRCONIUM AND HAFNIUM

By James B. Hedrick and David A. Templeton

1989

U.S. DEPARTMENT OF THE INTERIOR
BUREAU OF MINES

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ZIRCONIUM AND HAFNIUM

U.S.
DEPARTMENT
OF THE
INTERIOR

Manuel Lujan, Jr.
Secretary

BUREAU
OF
MINES

T S Ary
Director

October 1990

Contents

Legislation and Government Programs 1
Strategic Considerations 1
Production 1
Consumption and Uses 2
World Review 2
  Australia 2
  Bangladesh 4
  Denmark 4
  Guyana 4
  Madagascar 4
  Mozambique 4
  New Zealand 4
  Republic of South Africa 4
  Sierra Leone 5
  United Kingdom 5
Current Research 8
Outlook 9
Background 10
  Definition, Grades, and Specifications 10
  Industry Structure 10
  Geology-Resources 10
  Technology 10
Byproducts and Coproducts 11

COVER PHOTO:
The toughness of partially-stabilized zirconia is dramatized by demonstrations such as the one depicted here. Referred to as transformation-toughened zirconia (TTZ), this material withstands the blow of a hammer. (Photo credit: ASM International, Guide to Engineered Materials, Selecting Materials for Toughness. V. 3, No. 1, mid-June, 1988, p. 74.)

Tables

Table 1.—Salient U.S. Zirconium Statistics 2
Table 2.—Yearend Stocks of Zirconium and Hafnium Materials in the United States 2
Table 3.—Published Prices of Australian Zircon 3
Table 4.—Published Yearend Prices of Zirconium and Hafnium Materials 3
Table 5.—U.S. Exports of Zirconium, by Class and Country 5
Table 6.—U.S. Imports for Consumption of Zirconium and Hafnium in 1989, by Class and Country 8
Table 7.—World Annual Zirconium Mineral Production Capacity, December 31, 1989 8
Table 8.—Zirconium Mineral Concentrates: World Production, by Country 9

Figure

Figure 1.—Principal World Zirconium Minerals Producers 6

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ZIRCONIUM AND HAFNIUM

By James B. Hedrick and David A. Templeton

Messrs. Hedrick and Templeton are physical scientists with the Branch of Nonferrous Metals. They have shared coverage of zirconium and hafnium for about 2 years. Domestic survey data were prepared by Ms. Imogene P. Bynum, Nonferrous Metals Data Section.

Zirconium and hafnium occur together in nature at a ratio of about 50 parts zirconium to 1 part hafnium. Hafnium must be separated from zirconium that is to be used for certain nuclear applications but the two elements are used in combined form for most other applications.

Domestic production of zircon and zirconium oxide (zirconia) increased over that of the previous year. Two companies produced zircon as a coproduct of processing titanium minerals from three mines in Florida. Two companies in New Jersey recovered zircon from tailings previously accumulated as a byproduct during processing for ilmenite. The world production of zircon increased to a record-high level in 1989, but the supply continued to remain slightly below the level of demand. Zircon's strong demand in 1989 continued to result in historically high price levels.

Major uses for zirconium were in foundry sands, refractories, ceramics, abrasives, chemicals, and metallurgical applications. Hafnium was used in metallurgical applications, refractories, and ceramic cutting tools.

Advanced technology applications of zirconium included stabilized and partially stabilized zirconia used in extrusion dies, industrial cutting blades, ceramic engine parts, thermal barrier coatings for jet engines and other high-temperature environments, and radar transparent covers for radar equipment (radomes). Zirconium fluoride and hafnium fluoride glasses were used in fiber optics.

LEGISLATION AND GOVERNMENT PROGRAMS

Teledyne Wah Chang Albany (TWCA) requested Federal and State permission to dispose of low-level radioactive sludge generated by the pre-1980 refining of zirconium from zircon sand. The plans submitted for approval were prepared for TWCA by CH_2M-Hill, based in Corvallis, OR. The estimated 85,000 to 100,000 cubic yards of material, currently held in evaporation ponds, contains traces of uranium and thorium, and the decay products radium and radon. Previous findings concluded that the concentrations of these elements were insufficient to classify the waste as radioactive or hazardous. However, a Nuclear Regulatory Commission law disallowing the waste from being stored on a flood plain (Willamette River, 500-year) and public pressure prompted the company to seek disposal elsewhere. The plans included transport, via truck or rail, to a solid waste landfill, consolidation with Portland cement to prevent leaching, and disposal of the aggregate in a sealed structure. The Environmental Protection Agency (EPA) Record of Decision for Operable Unit #1 (Sludge Ponds) was signed at yearend, affirming the company plans. The EPA expected the estimated $10 million cleanup to commence in mid-1990.[1]

STRATEGIC CONSIDERATIONS

The National Defense Stockpile stocks of zirconium ore, totaling 14,507 metric tons, were classified as excess to goal. Zircon was produced in the United States, and there were no stockpile objectives for zirconium and hafnium materials.

Zircon was used in important defense related applications. Investment casting molds of zircon and zirconia were used to cast superalloy components of jet engines. Zirconia was used to form the crucibles in which superalloys were melted and in several other strategic applications, such as thermal barrier coatings on jet engine combustors and turbine vanes, as a white pigment for camouflage coatings in snow environments, and in sonar equipment for submarines.[2]

Zirconium was a minor constituent of many superalloys, and hafnium was a major component of an engine alloy used in the F-15 and F-16 military fighter planes. Both metals were required for use in U.S. Navy submarine nuclear reactors because of their dependability and performance in this application. At yearend 1989, the U.S. Department of Energy inventories were approximately 15 tons of zirconium sponge, 899 tons of zirconium ingot and shapes, 24 tons of zirconium scrap, 1 ton of zirconium crystal bar, 5 tons of hafnium oxide, 28 tons of hafnium ingot and shapes, and 3 tons of hafnium crystal bar.

PRODUCTION

Zircon was produced primarily as a coproduct or byproduct of processing heavy mineral sands for titanium minerals. Associated Minerals (USA) Inc., a subsidiary of the Australian firm Renison Goldfields Consolidated Ltd., produced zircon from heavy minerals mined and processed at Green Cove Springs, FL. E.I. du Pont de Nemours & Co. Inc. operated two mines near Starke and Lawtey in northeastern Florida that produced zircon and other heavy minerals. Heritage Minerals Inc. and Nord Ilmenite Corp. produced zircon from tailings that were previously generated during processing for ilmenite at Lakehurst and Jackson, NJ, respectively.

Molycorp Inc., a wholly-owned subsidiary of Unocal Corp., and the Mescalero Apache Tribe announced a joint

venture agreement to develop a deposit on the tribe's reservation in New Mexico. The deposit, identified by Molycorp in 1985, contains the mineral eudialyte, a zirconium- and yttrium-bearing silicate mineral. Reported reserves were 2.4 million metric tons grading 1.2% zirconium oxide and 0.18% yttrium oxide. Initial metallurgical tests by Molycorp indicated that the ore could be processed with conventional heap-leach technology, a low-cost process presently used by many gold and copper operations. Although Molycorp was engaged in the production and processing of yttrium and other rare earths for the past 20 years, zirconium would be a new addition to its product line. A schedule for development was not set.[3]

Piedmont Mining Company, Inc. was reportedly investigating occurrences of titanium minerals and zircon in North Carolina.

TAM Ceramics Inc., a subsidiary of the United Kingdom-based Cookson Group, began construction of a new facility at Niagara, NY, to produce zirconia using a recently developed chemical precipitation process. The new process, developed by Cookson Research, reportedly yields ultra-high purity zirconia using selective precipitation on an industrial scale. Completion of the new plant was scheduled for late 1990.[4]

CONSUMPTION AND USES

Apparent consumption of zircon in 1988 and 1989 was calculated by adjusting domestic production for net trade and changes in stocks. Prior to 1988, production data were withheld to avoid revealing proprietary data and consumption was estimated, based on a survey of the industry. The zircon consumption pattern, shown in the following table, was estimated based on survey data and were adjusted to equal total apparent consumption as rounded for 1988 and 1989. These data were not consistent with end use data published by the Bureau of Mines in prior years.

End use	1988[r]	1989
Zircon refractories[1]	29,000	23,000
AZS refractories[2]	15,000	12,000
Zirconia and AZ abrasives[3]	W	W
Alloys[4]	W	W
Foundry applications	50,000	41,000
Other[5]	60,000	50,000
Total	177,000	145,000

[r] Revised. W Withheld to avoid disclosing company proprietary data, included in "Total."
[1] Dense and pressed zircon brick and shapes.
[2] Fused cast and bonded alumina-zirconia-silica-based refractories.
[3] Alumina-zirconia-based abrasives.
[4] Excludes alloys above 90% zirconium.
[5] Includes chemicals, zirconium metal, welding rods, sandblasting, and other miscellaneous uses.

TABLE 1
SALIENT U.S. ZIRCONIUM STATISTICS
(Metric tons)

	1985	1986	1987	1988	1989
Zircon:					
Production:					
Concentrates	W	W	W	117,606	118,388
Milled zircon	42,744	46,970	42,394	64,393	54,994
Exports	15,291	15,852	20,054	[r]21,794	48,176
Imports for consumption	39,723	68,764	67,917	76,331	73,196
Consumption, apparent[1 2]	117,934	143,335	132,800	[r]176,991	144,813
Stocks, Dec.31: Dealers and consumers[3]	26,570	28,074	39,218	[r]34,370	32,965
Zirconium oxide:					
Production[e 4]	8,322	7,148	5,226	4,438	10,179
Exports	951	1,648	1,206	1,809	NA
Imports for consumption	1,332	464	1,274	1,089	NA
Consumption, apparent	6,804	6,078	3,800	[r]3,548	NA
Stocks, Dec. 31: Producers[e 4]	1,383	2,002	1,213	[r]1,383	1,767

[e] Estimated. [r] Revised. NA Not available. W Withheld to avoid disclosing company proprietary data.
[1] Includes insignificant amounts of baddeleyite.
[2] Please refer to the text under "Consumption and Uses" for a discussion of the apparent consumption of zircon.
[3] Excludes foundries.
[4] Excludes oxide produced by zirconium metal producers.

TABLE 2
YEAREND STOCKS OF ZIRCONIUM AND HAFNIUM MATERIALS IN THE UNITED STATES
(Metric tons)

Item	1988[r]	1989
Zircon concentrate held by dealers and consumers excluding foundries	31,522	26,966
Milled zircon held by dealers and consumers excluding foundries	2,848	5,999
Zirconium:[1]		
Oxide	1,383	1,767
Sponge, ingot, scrap, alloys	2,206	2,452
Refractories	6,202	5,383
Hafnium: Sponge and crystal bar[e]	27	27

[e] Estimated. [r] Revised.
[1] Excludes material held by zirconium sponge metal producers.

WORLD REVIEW

World capacity to produce zirconium minerals, shown in table 7, lagged demand by approximately 5%. Because of the strong and persistent demand for zirconium in both natural and processed forms, several deposits were in either the exploration, pilot plant, or development stage. The additional supplies provided by anticipated new and expanded operations should substantially ease the worldwide shortage of zircon.

Australia

The Nissho Iwai Corp. of Japan purchased RZ Mines (Newcastle) Ltd. and Cable Sands Pty. Ltd. for A$240 million from Pioneer International Ltd. Nissho had been importing rutile and zircon produced by RZ Mines for 20 years prior to the purchase. The company anticipated growth in demand for zircon resulting from Japan's increase in steel production and from the expanding European markets for fine ceramics. Combined, the two mining companies produced 50,000 to 60,000 tons of zircon per year, about 5% of world production.[5]

Cable Sands continued development of the Jangardup deposit in the southwest of Western Australia. The heavy

TABLE 3

PUBLISHED PRICES OF AUSTRALIAN ZIRCON

(U.S. dollars per metric ton)

Date of publication	Standard grade	Intermediate grade	Premium grade
December 1988	265–316	299–342	367–641
December 1989	395–474	395–474	474–790

Source: Industrial Minerals (London). No. 225, Dec. 1988, p. 83; and No. 267, Dec. 1989, p. 75.

TABLE 4

PUBLISHED YEAREND PRICES OF ZIRCONIUM AND HAFNIUM MATERIALS

Specification of material	1988	1989
Zircon:		
Domestic, standard-grade, f.o.b. Starke, FL, bulk, per short ton[1]	$242.00	$320.00
Domestic, 75% minimum quantity zircon and aluminum silicates, Starke, FL, bulk, per short ton[1]	161.00	204.00
Imported sand, containing 65% ZrO_2, f.o.b., bulk, per metric ton[2]	237.00– 259.00	435.00– 452.00
Domestic, granular, bags, bulk rail, from works, per short ton[3]	300.00– 350.00	300.00– 600.00
Domestic, milled, 200- and 325-mesh, rail, from works, bags, per short ton[3]	350.00– 450.00	350.00– 800.00
Baddeleyite, imported concentrate:[4]		
96% to 98% ZrO_2, minus 100-mesh, c.i.f. Atlantic ports, per pound	.51	.85– 1.05
99% + ZrO_2, minus 325-mesh, c.i.f. Atlantic ports, per pound	.91	1.16– 1.30
Zirconium oxide:[3]		
Powder, commercial grade, drums, 2,000-pound minimum, per pound	5.80– 5.85	2.00– 7.00
Electronic, same basis, per pound	8.50	3.50– 8.00
Insulating, stabilized, 325° F, same basis, per pound	4.50	4.50
Insulating, unstabilized, 325° F, same basis, per pound	5.00	5.00
Dense, stabilized, 30° F, same basis, per pound	3.00	3.00
Zirconium oxychloride: Crystal, cartons, 5-ton lots, from works, per pound[3]	.91– 1.04	.91– 1.04
Zirconium acetate solution:[3]		
25% ZrO_2, drums, carlots, 15-ton minimum, from works, per pound	.97	.97
22% ZrO_2, same basis, per pound	.78	.78
Zirconium hydride: Electronic-grade, powder, drums, 100-pound lots, from works, per pound[3]	.31– .75	.31– .75
Zirconium:[5]		
Powder, per pound	70.00– 150.00	70.00– 150.00
Sponge, per pound	12.00– 18.00	12.00– 18.00
Sheets, strip, bars, per pound	16.00– 45.00	16.00– 45.00
Hafnium: Sponge, per pound[5]	75.00– 135.00	75.00– 135.00

[1] E. I. du Pont de Nemours & Co. Inc. price lists. Oct. 1, 1988 and 1989 respectively.
[2] Industrial Minerals (London). No. 255, Dec. 1988, p. 83; and No. 267, Dec. 1989, p. 75.
[3] Chemical Marketing Reporter. V. 234, No. 26, Dec. 26, 1988 p. 26; and v. 236, No. 26, Dec. 29, 1989, p. 40.
[4] American Vermiculite Corp., Atlanta, GA. Baddeleyite price lists; and Ronson Metals Corp. price lists (effective Jan. 1, 1990).
[5] American Metal Market. V. 96, No. 253, Dec. 30, 1988, p. 6; and v. 97, No. 252, Dec. 30, 1989, p. 6.

mineral mine was expected to begin operation in 1990 or 1991, with an estimated capacity of 10,000 tons per year of zircon concentrate.

Production from Australmin Holdings Ltd. mine at Newrybar, New South Wales, was postponed because of an appeal by environmentalists to the Land and Environment Court. The appeal was not upheld and the company expected production to begin early in 1990. Processing of the 30,000 tons of concentrate expected to be produced annually will reportedly yield 10,000 tons of zircon and 12,000 tons of rutile.[6]

Associated Minerals Consolidated (AMC) Mineral Sands Ltd. began development of the Eneabba West deposit. The deposit, due to come onstream in 1990 or 1991, reportedly contains 230 million tons of sand with a heavy mineral grade of 3.1%. Projected annual production of zircon from Eneabba West was expected to reach 70,000 tons.

Two companies investigated heavy mineral deposits in the Scott River area of Western Australia. BHP-Utah Minerals International indicated that the Beenup deposit would be capable of dredging upwards of 500,000 tons of heavy mineral-bearing sand per year. The environmental impact on agricultural activity nearby was studied. A joint venture comprised of Golden Plateau NL, Kingsgate Consolidated Ltd., and Wynarde Pty. Ltd. found encouraging concentrations of ilmenite (39% to 64%), rutile (3% to 8%), and zircon (0.5% to 2%) on leases held in the vicinity. The overburden on the concentrated zones and slimes generated during the treatment phases were expected to present difficulties.[7]

North Broken Hill Peko Ltd. was evaluating the feasibility of the King Island, Naracoopa, mineral sand project. Total reserves were estimated to contain 25 million tons grading 5.2% heavy minerals. King Island is situated midway between Victoria and Tasmania near the Bass Strait.[8]

The Cooljarloo mineral sand deposit near Catabay, Western Australia, was expected to begin production near the end of the year. With reserves containing over 18 million tons of heavy minerals grading 12% zircon, the estimated 80% recovery rate should bring about one and three-quarter million tons of

zircon to market during the life of the mine. Zircon production expected in 1990 and 1991 was 31,000 and 67,000 tons, respectively. The Oklahoma City-based Kerr-McGee Chemical Corp. had a 50% interest in the venture through its Australian subsidiary KMCC Western Australia Pty. Ltd. The Australian firm Minproc Holdings Ltd. had equal equity in the project through its subsidiary Minproc Chemicals Pty. Ltd.

Mineral Deposits Ltd. planned to have a new mine near Bundaberg, Queensland, in operation by 1991. Initial output of zircon from this heavy mineral deposit, on the coast north of Rocky Point at Agnes Water, was projected to be 30,000 tons per year.[9]

The offshore portion of the Eastern Australian Rutile Province, encompassing the nearshore from Sydney north to the Queensland border, was found to contain over 2 million tons of zircon and rutile in noneconomic deposits as surveyed in the mid-1960's. New exploration for heavy minerals in the Province began in June on the nearshore of the continental shelf off the coast of New South Wales. The new marine geophysical survey includes sidescan sonar mapping and seismic reflection and magnetometer profiling; all data were to be digitized for high-resolution processing.[10]

Bangladesh

The Government was reported to have begun a mineral sands project which was previously discontinued. A survey of 240 square kilometers (km^2) of beach sands indicated heavy mineral resources totaling 420,000 tons. Minerals identified included titanium minerals, monazite, and zircon.[11]

Denmark

Morstral Minerals conducted exploratory drilling on an extensive (100 km^2) beach sand deposit exhibiting anomalous concentrations of zircon and other heavy minerals. The sands are located on the Thy Coast of the Jutland Peninsula in the vicinity of the Hanstholm Harbor.[12]

Guyana

An estimated 450 river-based diamond and gold dredges were reportedly processing heavy mineral-containing resources. Zircon and titanium minerals comprised the largest portion of the heavy minerals.[13]

Madagascar

QIT-Fer et Titane Inc. (QIT) indicated that problems mounting against the development of a mineral sand deposit, on the southeast coast in the Mandena region near Toalagnaro (formerly Fort Dauphin), would delay production until 1995. The ilmenite project, with reserves of 145 million tons, was a joint venture between QIT-Madagascar Mineral (49%) and the National Military Office for Strategic Industries (OMNIS), 51%. OMNIS reportedly initiated pilot plant construction, further exploration, and related industrial activity at the outset of the year. Annual zircon production of 24,000 tons was expected when fully operational.[14]

Mozambique

Kenmare Resources PLC of Ireland began the preconstruction and finance sourcing stage of its Congolone project after receiving approval from the Ministry of Mineral Resources to mine the deposit. Proven reserves of 167 million tons grading 3.25% heavy minerals were estimated to contain 373,000 tons of premium zircon. Beginning in early 1992, 37,000 tons per year of zircon were expected to be produced. Kenmare held a 71.25% equity in project, the Mozambican Government held 25%, and the geologic survey of Yugoslavia, Geoloski Zavod, which first explored the deposit, held 3.75%.[15]

New Zealand

In December, Fletcher Titanium Products Ltd. brought on stream a pilot mine located on the west coast of South Island. Combined production of 400 tons per year of monazite, rutile, and zircon was expected.[16] The possibility of more zircon production from South Island was to be decided upon the completion of a A$4 million feasibility study funded by Nissho Iwai Corp. of Japan, to be completed by May 1990. The study concerned a proposed titanium slag and pig iron plant at a 17-million-ton ilmenite deposit at Westport. Zircon, monazite, and gold would be byproducts of the operation.[17]

Republic of South Africa

Rhombus Mining (Pty.) Ltd. planned to develop a deposit to produce 27,000 tons of zircon per year. Drilling and seismic data on the heavy mineral sand deposit in the Transkei at Wavecrest, near the southeast coast, indicated reserves of 200 million tons grading 5% heavy minerals. Approval of the mining lease by the Department of Commerce, Industry, and Tourism was uncertain at yearend.[18]

The Anglo American Corp. of South Africa Ltd. studied the feasibility of developing heavy mineral sand deposits in Namaqualand. The deposits were on lands owned by De Beers Consolidated Mines near the west Cape coast, 30 miles north of the Olifants River. A wet concentration pilot plant was operated during the year. If a decision is made to proceed with the project, production was planned to commence in 1992, with expected annual zircon output of 100,000 tons per year. Rutile and monazite production were expected to be 25,000 and 1,000 tons per year, respectively.[19]

Severin Mining and Development Co. (Pty.) Ltd. conducted pilot plant tests in Australia on samples taken from a deposit it was exploring, 30 miles south of Richards Bay at Mitunzini. The deposit was reported to have a 10% heavy mineral grade resembling the Richards Bay Minerals deposit and a tentative mine life of 20 years. A decision was expected in early 1990, following completion and analysis of pilot plant tests.[20]

Richards Bay Minerals delayed exploration and development work on its project at Lake St. Lucia in the Natal Province because of environmental concerns. Although the company had reclamation practices which, according to the parent company QIT, "meet the highest standards for such operations anywhere in the world," environmentalists asked the International Union for Conservation of Nature to officially protect the area.[21]

Richards Bay Minerals received approval for the construction of a second dry mill which would double its zircon production to 300,000 tons per year by 1991–1992. The increase in raw feed material for the plant arises from the addition of two dredges in the past few years for a total of four. The company also planned to upgrade more of the standard grade zircon produced to an improved prime grade having a lower iron content than the prime grade previously produced.[22]

Sierra Leone

Australian mining companies, Intercontinental Gold & Minerals NL and MC Mining NL, expected to begin production of a heavy mineral deposit at Rotifunk in late 1990. Exploration of the deposit in the mid-1970's delineated reserves measuring 146 million tons grading 0.06% zircon (87,000 tons). The joint venture estimated production of 6,000 tons of zircon per year for 13 years. Rutile and ilmenite were to be the primary coproducts.[23]

Sierra Rutile Ltd. expected to begin zircon production of 15,000 tons per year in late 1990. Production is expected from stockpiled, zircon-rich tailings, and from a rutile deposit at Pejebu. Parent company Nord Resources Corp. recovered zircon from heavy mineral-rich tailings in New Jersey, in the United States. Following completion of the New Jersey project, operated by subsidiary Nord Ilmenite Corp., the company tentatively planned to dismantle and ship the separation plants to Sierra Leone to support these operations.[24]

United Kingdom

Butte Mining PLC, a precious and base metals producer, purchased Gramcol Zircon Ltd. for $6.6 million (£4 million).[25] Gramcol produced milled zircon for use as opacifiers in the ceramic industry. The company was reported to have a mill capacity of 1,500 tons per year.[26]

In a move to increase zirconium chemical production by one-third, Magnesium Elektron Inc. allocated $49 million (£30 million) for new plant construction and expansion of existing facilities at its manufacturing complex in Manchester. The company provided a full line of zirconium chemicals processed from raw zircon sand. Expansions were also planned for the company's facility in Flemington, NJ, in the United States.[27]

British Petroleum exited the mining business upon its sale of subsidiary BP Minerals Development Ltd. to the Rio Tinto Zinc Corp. PLC for $3.9 billion (£2.4 billion).[28] Rio Tinto Minerals Development Ltd. acquired total ownership of QIT-Fer et Titane Inc., which held 50% interest in a zircon producer, Richards Bay Minerals, in the Republic of South Africa. QIT tentatively planned to develop an ilmenite deposit in Madagascar.

TABLE 5

U.S. EXPORTS OF ZIRCONIUM, BY CLASS AND COUNTRY[1]

Class and country	1988		1989	
	Metric tons	Value (thousands)	Metric tons	Value (thousands)
Ore and concentrates:				
Argentina	840	$451	650	$679
Australia	171	155	261	1,893
Belgium	468	450	1,945	1,394
Brazil	—	—	538	943
Canada	386	157	2,979	1,456
Chile	—	—	90	200
Colombia	1,244	852	1,950	2,562
Costa Rica	—	—	140	93
Dominican Republic	—	—	201	176
Ecuador	276	269	779	757
Egypt	—	—	519	308
France	505	232	781	514
Germany, Federal Republic of	8,938	5,741	9,414	6,291
Guatemala	58	37	—	—
Guinea	88	29	—	—
Hungary	—	—	306	389
India	5	5	12	6
Indonesia	—	—	99	40
Ireland	18	3	38	9
Italy	14	6	5,874	1,623
Japan	776	141	3,388	1,748
Korea, Republic of	302	228	531	367
Mexico	6,346	2,662	8,327	4,760
Netherlands	109	103	1,041	759
Pakistan	—	—	53	102
Peru	—	—	18	45
Portugal	—	—	78	61
Spain	—	—	1,773	1,878
Taiwan	—	—	2,187	1,563
Thailand	88	65	18	34
U.S.S.R	—	—	1,234	610
United Kingdom	125	33	2,147	809
Uruguay	—	—	18	41
Venezuela	875	584	515	576
New Zealand	—	—	31	63
Other	162	137	241	410
Total	21,794	[2]12,339	48,176	33,139
Unwrought zirconium and waste and scrap:				
Belgium	36	321	36	394
Canada	9	89	14	316
France	7	64	—	—
Germany, Federal Republic of	3	50	6	54
Japan	61	2,704	83	3,050
Netherlands	14	48	—	—
Sweden	11	250	30	680
Switzerland	2	14	3	41
Taiwan	—	—	2	63
Thailand	—	—	7	179

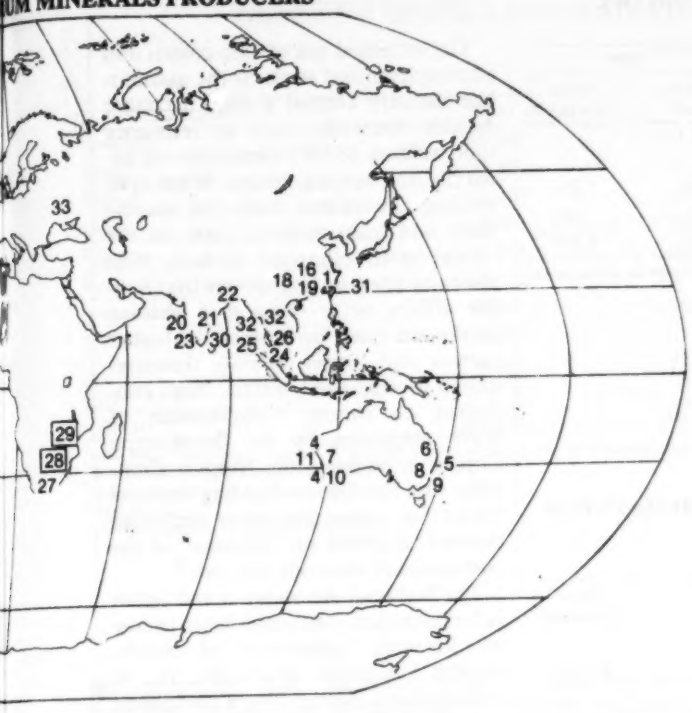
See footnotes at end of table.

FIG

PRINCIPAL WORLD ZIRCON

COMPANY	LOCATION
UNITED STATES	
1. E.I. du Pont de Nemours & Co. Inc.	Starke and Lawtey, Florida
2. Associated Minerals (USA) Inc.	Green Cove Springs, Florida
3. Heritage Minerals Inc.	Lakehurst, New Jersey
AUSTRALIA	
4. Associated Minerals Consolidated Ltd.	Capel and Eneabba, Western Australia
5. Consolidated Rutile Ltd.	Amity, Bayside, Gordon, Dunwich, and Pinkenba, Queensland
6. Currumbin Minerals Pty. Ltd.	Kirra, Kingscliff, Gympie, Gold Coast, Rainbow Beach, Cudgen, and Currumbin, Queensland
7. Cable Sands (WA) Pty. Ltd.	North Capel, Waroona, and Bunbury, Western Australia
8. Mineral Deposits Ltd.	Stockton, Durness, Hawks Nest, New South Wales
9. RZ Mines (Newcastle) Pty. Ltd.	Tomago and Nabiac, New South Wales
10. Westralian Sands Ltd.	North Capel, Yoganup, Yoganup North, and North Capel, Western Australia
11. TiO2 Corp. (Kerr-McGee Corp. and Minproc Holdings)	Cooljarloo, Western Australia (planned 1991)
BRAZIL	
12. Nuclebras de Monazita e Associados Ltda. (NUCLEMON)	Aracruz/Guarapari, Espirito Santo; Sao Joao da Barra, Rio de Janeiro; Usina de Santo Amaro, Sao Paulo
13. MINEGRAL	Aguas da Prata, Sao Paulo; Caldas and Pocos de Caldas, Minas Gerais
14. Rutilo e Ilmenita do Brasil Ltda.	Mataraca, Paraiba
15. Grupo Paranapanema	Presidente Figueiredo, Amazonas
CHINA	
16. State-owned	Yangjiang (Nanshanhai), Xitou, Dianbai, Zhanjiang, and Haikang, Guangdong Province
17. State-owned	Nangang, Guangdong Province

E 1
UM MINERALS PRODUCERS



LEGEND

Zirconium Minerals

Zircon	1-12, 14-27, 30-33
Baddeleyite	28, 29
Caldasite	13

COMPANY	LOCATION
CHINA (cont'd)	
18. State-owned	Qinzhou and Beihai, Guangxi Province
19. State-owned	Sai-Lao, Wuznaung, and Xinglong, Hainan Island
INDIA	
20. Indian Rare Earths Ltd.	Chavara, Alwaye, Kerala
21. Indian Rare Earths Ltd.	Manavalakuruchi, Tamil Nadu
22. Indian Rare Earths Ltd.	Chatrapur, Orissa
23. Kerala Minerals & Metals Ltd.	Chavara, Kerala
MALAYSIA	
24. Malaysian Mining Corp. Berhad	Various locations in Perak and Selangor States
25. Beh Minerals Sendirian Berhad	Lahat, Perak
26. Others	Various locations
SOUTH AFRICA	
27. Richards Bay Minerals	Richards Bay, Natal
28. Palabora Mining Co.	Palabora, Transvaal
29. Phosphate Development Corp. (Foskor)	Palabora, Transvaal
SRI LANKA	
30. Ceylon Mineral Sands Corp.	Pulmoddai
TAIWAN	
31. Pacific Ocean Rare Earth Industry	Yuanlin and Chiai Counties
THAILAND	
32. Various companies	Prachuap Khiri Khan, Chumphon, Phuket, and Takua Pa
U.S.S.R.	
33. State-owned	Verkhnednepravskiy complex Dnepropetrovsk Oblast

TABLE 5—Continued

U.S. EXPORTS OF ZIRCONIUM, BY CLASS AND COUNTRY[1]

Class and country	1988		1989	
	Metric tons	Value (thousands)	Metric tons	Value (thousands)
Unwrought zirconium and waste and scrap—Continued				
United Kingdom	20	100	43	1,011
Other	2	71	18	209
Total	165	[2]3,712	242	5,997

[1] Because of the implementation of the Harmonized Tariff System in Jan. 1989, export categories for 1989 are not necessarily comparable to those of previous years.
[2] Data do not add to total because of independent rounding.

Source: Bureau of the Census.

TABLE 6

U.S. IMPORTS FOR CONSUMPTION OF ZIRCONIUM AND HAFNIUM IN 1989, BY CLASS AND COUNTRY[1]

Class and country	Metric tons	Value (thousands)
Zirconium ore and concentrates:[2]		
Australia	51,445	$21,149
Belgium	18	13
Canada	111	24
Germany, Federal Republic of	51	43
Malaysia	250	263
South Africa, Republic of	20,832	11,840
United Kingdom	416	569
Other	73	59
Total[3]	73,196	33,958
Zirconium, unwrought and waste and scrap:		
Canada	10	12
France	10	53
Germany, Federal Republic of	35	352
Japan	57	446
United Kingdom	39	387
U.S.S.R.	91	740
Other	26	120
Total	268	2,110
Hafnium, unwrought and waste and scrap:		
France	4	806
Germany, Federal Republic of	(4)	151
Switzerland	(4)	19
Total	4	976

[1] Because of the implementation of the Harmonized Tariff System in Jan. 1989, import categories for 1989 are not necessarily comparable to those of previous years.
[2] Excluding Australia, Malaysia, and the Republic of South Africa, countries are believed to be point of shipment rather than point of origin.
[3] Data may not add to totals shown because of independent rounding.
[4] Less than 1/2 unit.

Source: Bureau of the Census.

CURRENT RESEARCH

The increased use of zinc-coated and electrogalvanized steels by the automobile industry created a need for more durable electrodes such as resistance spot welding (RSW) electrodes on assembly line welding robots. When spot welding zinc-coated steel, the coating melts and brass tends to form on the copper-based electrode surface, thus affecting integrity and service life. Similar affects occur when spot welding galvanized steels because of the higher current and longer welding times required to weld these metals. Tests conducted on various compositions of RSW electrodes by an Outokumpu Copper subsidiary, the Nippert Company, and the Edison Welding Institute found that copper-zirconium electrodes showed "superior performance" in the conventional electrode life test.[29]

The National Aeronautics and Space Administration contracted Basic Industry Research Laboratory of Northwestern University, Evansville, IL, to evaluate wear characteristics on coating materials for eventual use on the main-engine bearings of the space shuttle. Among the many materials to be tested

TABLE 7

WORLD ANNUAL ZIRCONIUM MINERAL PRODUCTION CAPACITY, DECEMBER 31, 1989

(Thousand metric tons)

Country	Rated capacity[1]
Australia	550
Brazil[2]	22
China[e]	35
India	16
Malaysia	12
South Africa, Republic of[3]	190
Sri Lanka	6
Thailand	2
United States	130
U.S.S.R.[e]	30
Total (rounded)	1,000

[e] Estimated.
[1] Capacity for the zirconium minerals, zircon, baddeleyite, and caldasite.
[2] Includes 500 tons of capacity for caldasite.
[3] Includes 20,000 tons of capacity for baddeleyite.

TABLE 8

ZIRCONIUM MINERAL CONCENTRATES: WORLD PRODUCTION, BY COUNTRY[1]

(Metric tons)

Country	1985	1986	1987	1988[p]	1989[e]
Australia	501,440	451,824	456,590	480,049	546,000
Brazil[2]	21,039	15,116	18,140	r e19,000	19,000
China[e]	15,000	15,000	15,000	15,000	15,000
India[e]	3 14,800	16,000	r10,000	r15,000	16,000
Malaysia	11,652	12,633	17,828	25,671	19,700
South Africa, Republic of[e 4]	3 160,533	140,000	140,000	150,000	160,000
Sri Lanka[e]	3 4,061	4,000	4,000	4,000	4,000
Thailand	1,292	1,705	1,532	5,098	5,000
U.S.S.R.[e]	85,000	85,000	r90,000	r90,000	90,000
United States	W	W	W	117,606	3 118,388
Total	814,817	741,278	753,081	921,424	993,088

[e] Estimated. [p] Preliminary. [r] Revised. W Withheld to avoid disclosing company proprietary data; excluded from "Total."

[1] Includes data available through May 9, 1990.

[2] Includes production of zircon and caldasite.

[3] Reported figure.

[4] Includes production of zircon and baddeleyite.

are zirconium- and hafnium-nitride hard film coatings and nitride alloys of titanium and zirconium. The coatings were to be developed via a high-rate reactive sputtering process and deposited in vacuo within a reactor vessel.[30]

A new mill developed by Metprotech, based in the Republic of South Africa, for increasing the recovery of gold from refractory ores was reported to reduce the milling time required to mill zircon. The mill, which has a throughput range of 2 to 4.5 tons per hour, incorporates a horizontal central arm which stirs both feed material and grinding balls within a cylindrical drum.[31]

The Bureau of Mines sponsored research which identified a zirconium-nickel compound that may possibly substitute for the platinum-group metals catalysts currently used in automobile emission control systems.[32]

A new zirconia-alumina ceramic was developed by Diamonite Products of W. R. Grace & Co. The flexural strength was reported to be twice that of 87% alumina, accompanied by a five-fold increase in wear resistance. These qualities combined with its resistance to chemical attack made it an ideal candidate for industrial applications including mineral handling and processing. The ceramic was said to be capable of fabrication by many different processes.[33]

Sumitomo Metal Industries, Ltd. of Japan produced zirconium-manganese alloys for hydrogen storage. The high-frequency melted, coarse alloy powders absorb and desorb hydrogen between 200° C and 300° C and perform effectively after many cycles. The new alloy was reported to work faster and cost less than lanthanum-nickel alloys.[34]

A new zirconia-based thermal barrier coating was developed by Woking, United Kingdom-based Metco Ltd. which reportedly outperformed standard yttria-stabilized zirconia thermal coatings. Incorporating 24% to 26% cerium, 2% to 3% yttria, and the balance zirconia, the coating was claimed to have more resistance to cyclic thermal fatigue, less susceptibility to hot corrosion and erosion, lower thermal conductivity, and more predictable performance. Standard stabilized zirconia coatings (i.e., calcia-, magnesia-, and yttria-stabilized) have proven to be efficient thermal barriers in clean fuel environments; however, fuel contaminated with chlorine, sodium, sulphur, and/or vanadium adversely affect the performance of the coating. The company used its own plasma spray process to apply hollow, spherical particles to form the coating. This development was related to work initiated by U.S. parent company Perkin-Elmer Corp.[35]

OUTLOOK

Exploration and development of heavy mineral deposits in recent years was expected to lead to development of several new zircon mines by the early 1990's. The increase in production from planned, new, and expanded operations was expected to ease the supply shortages experienced in the late 1980's. An increase in world production of about 100,000 tons, or 10% of current world production, was expected by 1991. The near-term affect on zircon prices will likely be downward; however, it also was possible that increased availability of processed materials could create new demand pressures and prices could remain high.

New uses for zirconia grew dramatically in recent years. Substantial increases in consumption of this material in end products, ranging from scissor and knife blades to wear-resistant bearings and oxygen sensors, are expected in the next few years. Growth of wear-resistant ceramics and composites for the coming decade have been estimated at 18% to 23%.[36] Certain niches of the tungsten cutting tool market have already been penetrated by ceramics and ceramic-metal composites, some of which contain zirconia. Stabilized zir-

conia thermal barrier coatings are becoming the mainstay of commercial and military turbine engine components. The added costs of manufacture are negligible considering the added performance and extended service life.

A multimillion dollar expansion being implemented by one of the largest zirconium chemical producers foreshadowed growth in this area.

The supply side outlook for zircon is rather encouraging. The demand for other heavy minerals, such as ilmenite and rutile to make titanium dioxide (white pigment) and metal, is very strong and expected to remain so. Also, there is no slack in demand foreseen regarding the rare earths and hence the source mineral monazite. As these minerals are the marketable products of most heavy mineral mining operations, there appears to be adequate incentive for mining companies to fully exploit existing deposits and to continue with exploration and development efforts.

The world reserve base for zircon was conservatively estimated to be about 75 million metric tons. At the current rate of production this is ample supply for nearly 75 years.

BACKGROUND

Definition, Grades, and Specifications

Zirconium and hafnium are chemically similar elements with atomic numbers 40 and 72, respectively. Both elements are classified in the periodic table as members of Group 4b, and have only one oxidation state, +4, and have similar ionic radii. Owing to these similar properties, zirconium and hafnium are usually found together in nature.

Zircon purity is commonly measured by the combined zirconium dioxide (zirconia) and hafnium dioxide (hafnia) content. Hafnium occurs in zircon in a typical ratio of 1 part hafnium to 50 parts zirconium. Commercially available zircon typically grades 64.5% to 66% combined zirconia-hafnia. Zircon grades are similar on a worldwide basis, but no standard requirement exists. Standard grade zircon has a typical analysis of 65% minimum zirconium dioxide-hafnium dioxide, 0.25% maximum titanium dioxide, and 0.12% maximum iron oxide. Intermediate grade zircon has a typical analysis of 65.5% zirconium dioxide-hafnium dioxide, 0.03% maximum titanium dioxide, and 0.1% maximum iron oxide. Premium grade zircon has a typical analysis of 66% minimum zirconium dioxide-hafnium dioxide, 0.1% maximum titanium dioxide, and 0.05% maximum iron oxide.

Zirconium metal for the chemical process industry is available in three American Society for Testing and Materials (ASTM)-approved grades: R60702 for unalloyed zirconium, R60704 for the tin-iron alloy, and R60705 for the niobium alloy. Zirconium alloys for the nuclear industry, the compositions of which are specified, are designated as Zircaloy-2, Zircaloy-4, or Zr-2.5 Cb.

Hafnium metal as produced by the Kroll process is called hafnium sponge or "Kroll-process" sponge or metal. After refining by the iodide process, the metal is called crystal bar.

Industry Structure

Zirconium ore minerals are sold by mine producers directly to processors, consumers, and commodity brokers. Primary ore concentrate of zircon and baddeleyite may be used in certain industrial uses with little or no processing, but most applications require additional processing. Processors grind the concentrates to specification for certain applications or convert zircon and baddeleyite to refined products such as zirconium metal, hafnium metal, alloys, high-purity zirconia, and other compounds. Extensive processing is required to produce ultrapurity powders and nuclear-grade metals. Processors producing oxide and metal are often partially integrated, and market fabricated and semi-fabricated products directly to manufacturers. The worldwide distribution of the mining industry is illustrated in figure 1.

Geology-Resources

Zircon is a common accessory mineral in igneous rocks. It is frequently found associated with silicic rocks, including granite, granodiorite, syenite, monzonite, and nepheline syenite. Zircon is also found in pegmatites, crystalline limestone, and the metamorphic rocks gneiss and schist. One occurrence of zircon is reported from a meteorite. From an economic viewpoint, sedimentary placer deposits are the most significant.

Placer deposits begin forming when chemical and mechanical weathering liberates minerals from the source rock. This is followed by transport of the minerals to the sea by water, wind, and gravity. Upon reaching the sea, deposits of economic value form primarily by hydraulic sorting. Heavy minerals, including zircon, are concentrated by marine currents and wave action. Mechanical sorting by the sea and wind further sorts the grains to produce well-sorted beach deposits.

With distance from the source, zircon undergoes varying degrees of rounding, but because of its hardness typically retains an elongate shape with rounded edges and high relief. If sufficient source material exists, an economic heavy mineral deposit forms. Zircon and other heavy minerals are primarily recovered as sand ranging in size from very fine to coarse.

Technology

Economic concentrations of zircon are found in association with other heavy minerals such as ilmenite, rutile, and monazite. Heavy mineral sand deposits are usually mined by floating cutterhead- or bucketwheel-dredges that handle up to 2,800 metric tons of sand per hour. Sand recovered by these techniques is sent to a wet mill and treated by wet-gravity methods, using spirals, cones, sluices, or jigs, to produce a mixed heavy mineral concentrate containing zircon. The mixed concentrate typically contains other economic minerals such as the titanium minerals (ilmenite, rutile, and leucoxene) and oftentimes smaller amounts of the rare-earth mineral monazite. In southeast Asia, heavy mineral sand deposits containing zircon are mined primarily for the tin minerals cassiterite and stannite.

The mixed heavy mineral concentrate is scrubbed, dried, and screened, and the individual heavy minerals are separated by electrostatic, electromagnetic, magnetic, and gravity processes. Zircon, in contrast to ilmenite, rutile, and many other heavy minerals, is nonconductive and can be separated along with monazite, by electrostatic methods. Monazite, which is slightly magnetic and may be slightly higher in specific gravity, can be separated from zircon by electromagnets or by additional gravity methods.

To obtain premium grade zircon, the zircon concentrate from the electrostatic-

electromagnetic circuit is again subjected to gravity concentration to reduce the content of aluminum- and titanium-bearing minerals. Certain zircon products are leached in an acidic solution to remove iron oxide and other grain coatings.

Zircon used in foundry and certain refractory applications is graded, sized, and, in many cases, ground or milled to produce zircon flour. Foundry applications generally use zircon sand and flour mixtures, which may be treated with resin coatings and binders.

Zirconia is produced directly from zircon by either plasma fusion or electric arc techniques. The plasma method for zirconia production employs heating a finely divided zircon above its dissociation temperature to form small zirconia crystallites and glassy amorphous silica. The hot zirconia and silica particles are rapidly quenched, and the silica removed by leaching with sodium hydroxide, leaving insoluble zirconia crystallites.

In electric arc production, zircon is heated to temperatures of approximately 2,500° C producing dissociation. The silicon component is vaporized and recovered as fumed silica leaving a residual zirconia melt that is rapidly air quenched to form spherules. A more complex electric arc method melts a mixture of limestone and zircon to form calcium zirconate and tricalcium silicate clinker. Cooling of the mixture disintegrates the mixture into a very fine powder composed of tricalcium silicate and lime and a coarser fraction of calcium zirconate crystals. The calcium zirconate is separated from the other constituents by either air classification or flotation. The acid-soluble calcium zirconate crystals are treated with acids or other reagents forming zirconia or zirconium salts.

Other compounds of zirconium, such as the hydrous or carbonated oxide, acetate, sulfate, fluoride, chloride, and organic complexes are usually prepared from zirconia or its salts by chemical reactions.

The deBoer-van Arkel iodide process, first described in 1925, is essentially a refining process and was commercially adopted in 1945 as the first practical method for producing ductile zirconium metal. Zirconium metal is reacted with iodine vapor at 200° C to form zirconium tetraiodide, leaving most impurities except hafnium in a solid state. The gaseous halide diffuses to a heated filament where, at 1,300° C, the reaction is reversed, depositing very high-purity elemental zirconium on the filament and regenerating iodine vapor for reuse. The process yields high-purity metal but is expensive to operate.

Industrial scale plants for producing zirconium metal are based on the Kroll process in which zirconium tetrachloride is reduced with molten magnesium in an inert atmosphere. The resulting mixture of zirconium metal sponge and magnesium chloride is vacuum-distilled to remove the magnesium chloride. The zirconium is crushed, sized, and compacted to form a consumable electrode. The electrode is arc-melted in an inert atmosphere to give a first-melt ingot. The first-melt ingot is then used as a consumable electrode to produce a metallurgically homogeneous second-melt ingot, which is machined to give a clean surface and readied for fabrication.

Zirconium tetrachloride is produced by chlorinating zircon sand in a fluidized bed containing carbon at a temperature of about 1,150° C.

BYPRODUCTS AND COPRODUCTS

Zircon is mined from deposits with a heavy mineral grade between 2% and 20%. The associated economic heavy minerals are ilmenite, leucoxene, rutile, monazite, and the tin minerals cassiterite and stannite. Its classification as a byproduct or a coproduct depends on the fraction of zircon in relation to the other minerals. If zircon and the titanium minerals are expected to account for the majority of the revenue, it is considered a coproduct. If minerals other than zircon provide the carrying costs of the operation, then zircon is considered a byproduct. Small quantities of baddeleyite are recovered as a byproduct of copper, phosphate, and vermiculite mining in the Republic of South Africa.

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